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Optical Birefringence in Cubic Crystals

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When there exists a nonlocal relation between polarization and electric field $\mathbf{E}$ in a cubic crystal, the dielectric tensor ϵ_{ij} appropriate to a light wave with propagation constant $\mathbf{k}$ has the form [1, p. 96f]:

$$\epsilon_{ij} = \epsilon_0 \, \delta_{ij} + \sum_{r,m} \alpha_{ijrm} k_r k_m \,. \tag{1}$$

When this ansatz is substituted into Maxwell's equations, the $O(k^2)$ terms cause the phase velocity to depend on wave polarization, so that we have bi-refringence if $\mathbf{k}$ is not parallel to a symmetry axis [1, 2].

The detailed dependence of k and refractive index $\tilde{n}$, for a propagating mode of given polarization, on $\mathbf{s} \equiv \mathbf{k}/k$ has been predicted several times [1, 3, 4] by invoking the contribution to ϵ_{ij} of exciton transitions induced by the $\mathbf{p} \cdot \mathbf{A}$ interaction between an electron of momentum $\mathbf{p}$ and a field of vector potential $\mathbf{A}$. For a plane, transverse electromagnetic wave with $\mathbf{E}/E \equiv \boldsymbol{\xi}$, we expand

$$\mathbf{A} = -\frac{ic}{2\omega} \boldsymbol{\xi} \{ E_0 \exp[i(\mathbf{k} \cdot \mathbf{r}) - \omega t] - \text{c.c.} \}$$

and consider transitions caused by the quadrupole $O(k)$ contribution to $H_{\text{int}} = -e(2mc)^{-1}[\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}]$. The probability of such a transition from ground state $| \, 0 \rangle$ to state $| \, S \rangle$ should be proportional to the absorption or radiative intensity

$$I = |\langle S \mid H_{\text{int}} \mid 0 \rangle|^2 = Bk^2 \mid \boldsymbol{\xi} \cdot \langle S \mid \mathbf{pr} \mid 0 \rangle \cdot \mathbf{s} \mid^2 \tag{2}$$

which gives the $\mathbf{s}$ dependence of both absorption and $\tilde{n}^2$.

Existing calculations [1, 3, 4] based on (2) have selected a 4-fold axis as the direction of unit vector $\mathbf{z}$ and taken $\boldsymbol{\xi}$ to be either of

$$\boldsymbol{\xi}_s = (\mathbf{s} \times \mathbf{z}) \mid \mathbf{s} \times \mathbf{z} \mid^{-1}, \qquad \boldsymbol{\xi}_p = \mathbf{s} \times \boldsymbol{\xi}_s \,. \tag{3}$$

If this choice has any physical meaning, these waves must be the unique transverse pair that can propagate in a general direction in an anisotropic crystal (see below). In terms of the cartesian components $[\cos\theta, \sin\theta\cos\phi, \sin\theta\sin\phi]$ of $\mathbf{s}$, the functions I appropriate to "s" and "p" polarization, for $| S\rangle$ a doubly-degenerate excited state, assume the form [1, p. 167],

$$\begin{aligned} I_s &= B_s \sin^2\theta \sin^2 2\phi, \\ I_p &= B_p \sin^2 2\theta(3 + \cos^2 2\phi). \end{aligned} \tag{4}$$

These intensities are not invariant as they should be with respect to rotations about a trigonal axis, and therefore there must be additional transverse waves, which we shall see is not the case, or else the existing literature [1, 3, 4] has gone astray. For if we set $I_s = I_p$, we find $\theta = 0$ is an isolated point satisfying this isotropy condition whereas $\theta = \pi/2$, $\phi = 0$ lies on a continuous $I_s = I_p$ curve passing through it.

Clearly the error lies in the choice (3) for $\boldsymbol{\xi}$. We can always find two orthogonal directions $\boldsymbol{\xi}_1$, $\boldsymbol{\xi}_2$ such that $I_1 = I_2$ when we calculate I from (2), and so if we do not get optical isotropy in a direction $\mathbf{s}$ in which it should occur by cubic symmetry, we have simply made the wrong choice of $\boldsymbol{\xi}$ for that direction. Equations (3) are appropriate for a crystal in which $\mathbf{z}$ is the unique optic axis, where an O_h cube has seven axes, in $\langle 001\rangle$ and $\langle 111\rangle$ directions.

To determine the two correct $\boldsymbol{\xi}$ values for a given $\mathbf{s}$, we must go back to Maxwell's equations and derive [1, p. 153]:

$$\tilde{n}^2 E_i = [\epsilon_0 + \alpha_2 \tilde{n}^2]\, E_i + \tilde{\alpha}\tilde{n}^2 s_i^2 E_i + (2\alpha_3 + 1)\, \mathbf{E}\cdot\mathbf{s}\, \tilde{n}^2 s_i, \qquad i = 1,\ldots, 3, \tag{5}$$

where α_1, α_2, α_3 are the three nonzero components of α_{ijrm}, and

$$\tilde{\alpha} = \alpha_1 - \alpha_2 - 2\alpha_3 .$$

If we set $\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1$, where $\mathbf{E}_0 = E_0\, \mathbf{e}$ is transverse and $\mathbf{E}_1$ is a small longitudinal component which we calculate to $0(\alpha)$, treating the α term in (5) as a perturbation, we find

$$\begin{aligned} \tilde{n}^2/\epsilon_0 &= 1 + \alpha_2 + \tilde{\alpha} \sum_j s_j^2 e_j^2, \\ s_i^2 e_i - e_i \sum_j s_j^2 e_j^2 &- s_i \sum_j s_j^3 e_j = 0. \end{aligned} \tag{6}$$

These equations are satisfied by $\mathbf{e}$ directions (3) only in symmetry planes containing $\mathbf{z}$ or perpendicular to $\mathbf{z}$. Therefore, Eqs. (4) are physically meaningless except in these planes. Since $\tilde{\alpha}$ is only a proportionality factor in the angle-dependent terms, the relative anisotropy corresponding to different **s** directions resulting from existence of two solutions to Eqs. (6) is independent of the α_i, and therefore of $| S\rangle$, so long as $\tilde{\alpha} \neq 0$, which is true except for one triply-degenerate $| S\rangle$. A more detailed description of these calculations will be given in a later paper.

References

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